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Forced-Flow Chromatography of Alkali Earth Ions Detected by Photometric Method

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Forced-flow chromatography on a cation-exchange resin was used to obtain rapid separation and sensitive quantitation of alkali earth ions, Mg, Ca, Sr, and Ba. The resin provided the easy separation of alkali earths by using sodium chloride as an eluent, and on-stream addition of a color-forming reagent, *o*-cresol phthalein complexone, provided the continuous detection and quantitation of the eluted alkali earths. Linear relations were obtained in the range of 0.1 to 1 μ g magnesium, 0.05 to 2 μ g calcium, 0.5 to 10 μ g strontium and 5 to 100 μ g barium.

KEY WORDS: Forced-flow chromatography/ Alkali earth/

INTRODUCTION

Ion exchange has been successfully applied to the separation of the inorganic ions for many years. Recently, the advances of forced-flow liquid chromatography has made the high-speed separation of the inorganic ions possible. Coulometry¹⁾, radioactivity measurements²⁾, spectrophotometry^{3~5)} and flame photometry⁶⁾ were used as the detection method of the chromatography. Of these detection methods the spectrophotometry is most popular and can determine many metals sensitively by using a very sensitive color reagent. In this paper, for the rapid separation of alkali earths forced-flow liquid chromatography on the cation exchange resin was used, and by the on-stream addition of *o*-cresol phthalein complexone, PC, as the color forming reagent, the eluted alkali earth ions were detected continuously.

EXPERIMENTAL

Apparatus

The Pyrex column (2 mm i.d. \times 220 mm in length) was equipped with a Yanagimoto liquid chromatograph Model L-1030 and filled with Hitachi custom ion exchange resin 2611. Kyowa Seimitsu quartz window flow cell having 8 μ l in volume and 10 mm in light pass, was equipped with Hitachi 139 spectrophotometer as a detector of the liquid chromatograph. Absorbance curves of alkali earth complexes were measured with a Model 323 Hitachi recording spectrophotometer with 1.0 cm cells.

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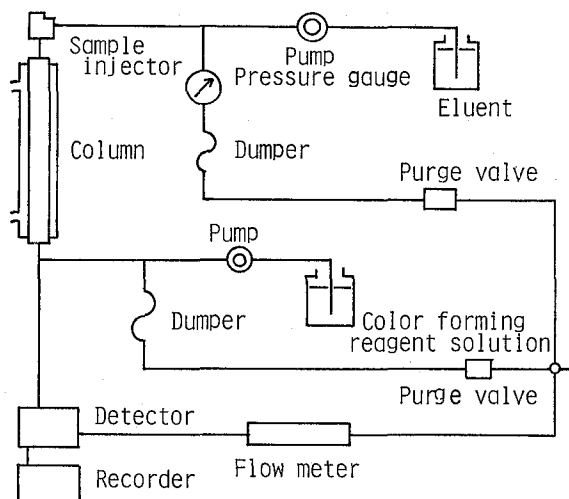


Fig. 1. Schematic diagram of liquid chromatograph.

Reagents and Procedure

A schematic diagram is shown in Fig. 1. The solutions of sodium chloride ranging from 1.5 to 3.0 M were used as the eluent. The sample solution of alkali earths was injected through a septum rubber by a Hamilton microsyringe, and the elution was performed keeping the temperature of the Pyrex column at 60°C by using water jacket. Then the color forming solution was added in the eluted solution by Kyowa Seimitsu mini-micro pump KHU-26(H), and the absorbances were measured at 570 nm after the color was developed between alkali earth ions and PC. Flow rate of the eluent and the color forming solution was 0.42 and 0.86 ml/min, respectively. The color forming solution contained 6×10^{-5} M of PC, 1 M of ammonia-ammonium chloride buffer, 10.5 of pH and 7.5 volume % of methanol. *o*-Cresol phthalein complexone (PC) was purchased from the Dojindo Co. Ltd., Research Laboratories. All the chemicals used in the experiment were reagent grade materials.

RESULTS AND DISCUSSION

Spectra of PC Complexes

o-Cresol phthalein complexone, which is used as an indicator of chelatometric titration for alkali earth metals, is not very suitable for a photometric reagent because of its fading in the aqueous solution.⁷⁾ But there is little problem for the liquid chromatograph detection system owing to the constant and considerably short lapse of time until the detection of the color development. Figure 2 shows the spectra of PC complexes of magnesium, calcium, strontium, and barium measured under the same conditions as the solution in the flow cell. As seen in the figure, it seems suitable to make the measurements at the wave length of 570 nm, where there exists a mean maximum wave length of the complexes. Measurements were, therefore, performed at 570 nm in the following experiments.

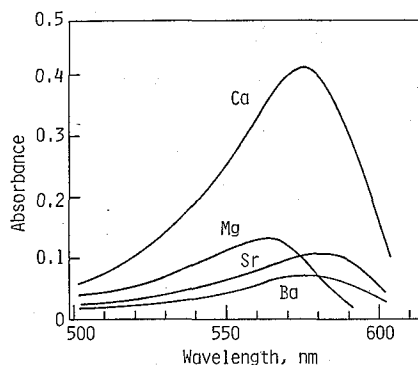


Fig. 2. Absorption spectra of PC complexes.

Alkali earth ion; 2×10^{-5} M, PC; 4×10^{-5} M, MeOH; 5%, ammonia-ammonium chloride buffer (pH 10.6); 0.7 M, NaCl; 0.8 M.

Addition of Methanol

When the alkali earth ions are titrated chelatometrically with ethylenediamine tetraacetic acid (EDTA) using PC as a metallochromic indicator, methanol is usually added into the titrated solution to repress the color change of the blank solution and to stabilize that of the sample solution. Figure 3 indicates the effect of the methanol content on the absorbance of calcium complex at 570 nm. As the methanol content increased in the sample solution, the stability in the color development of the PC complex increased, but the sensitivity of the complex fairly decreased. Five per cent of the methanol content was, therefore, adopted by considering the sensitivity and stability of the complex.

Effect of pH

The spectra of the complexes changed with the value of pH. The effect of pH on the absorbances of the PC complexes with alkali earth ions was, therefore, examined over the pH range 9.5–11. The result is shown in Fig. 4. As the pH value in the

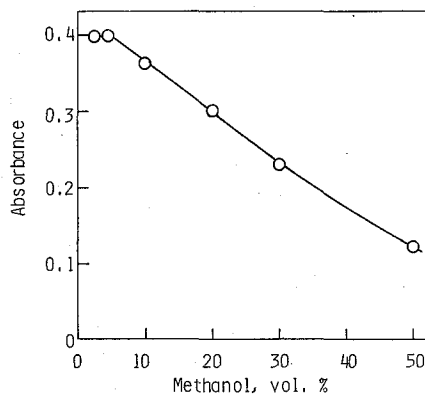


Fig. 3. Effect of methanol on the absorbance of calcium complex. PC; 4×10^{-5} M, Ca; 2×10^{-5} M, NaCl; 0.8 M, ammonia-ammonium chloride buffer (pH 10.6); 0.7 M.

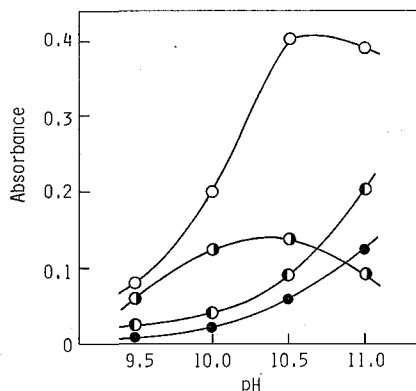


Fig. 4. Effect of pH on the absorbance of PC complexes. Alkali earth ion; 2×10^{-5} M, PC; 4×10^{-5} M, MeOH; 5%, ammonia-ammonium chloride buffer; 0.7 M, NaCl; 0.8 M. (○; Mg, ○; Ca, ◐; Sr, ●; Ba.

sample solution increased, the absorbance of the barium and strontium complexes increased gradually. On the other hand the absorbances for the complexes of the other alkali earth ions, magnesium and calcium had a maximum value at 10.5 of pH. Taking this result into account, the pH value for color forming was kept at 10.5 throughout the following experiments.

Effect of Eluent Concentration

Ammonium acetate¹⁾, hydrochloric acid⁸⁾, ammonium lactate⁹⁾ and ammonium chloride¹⁰⁾ were used as the eluents for alkali earth ions. In this experiment sodium chloride was adopted because the pH value of its eluted solution can be easily adjusted by the addition of the buffer solution. Figure 5 indicates the relationship between the

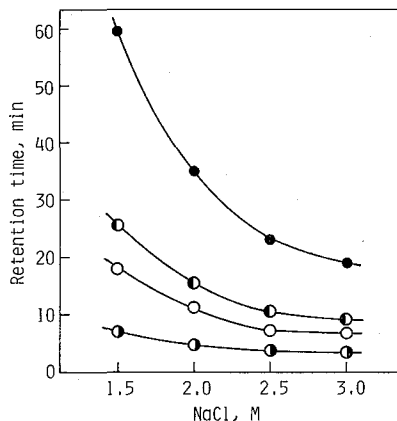
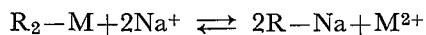


Fig. 5. Effect of sodium chloride concentration in eluent on retention time. Color forming reagent solution; 6×10^{-5} M PC, 7.5% MeOH, 1 M ammonia-ammonium chloride buffer (pH 10.6). Flow rate; 0.42 ml/min in eluent, 0.86 ml/min in color forming reagent solution. (○; Mg, ○; Ca, ◐; Sr, ●; Ba.

retention time of alkali earth and the concentration of sodium chloride. An equilibrium is considered to hold fairly good between the cation exchange resin and the eluent as follows,



where M stands for alkali earth ion, and R denotes a functional group of the cation resin. For this reason, the retention time of alkali earth ion decreased as the concentration of sodium chloride increased.

The addition of over 3 M of sodium chloride made worse the separation of calcium and strontium ions and also made insufficient the color development of the magnesium complex. Considering the separation time and the separation factor, 2.5 M of sodium

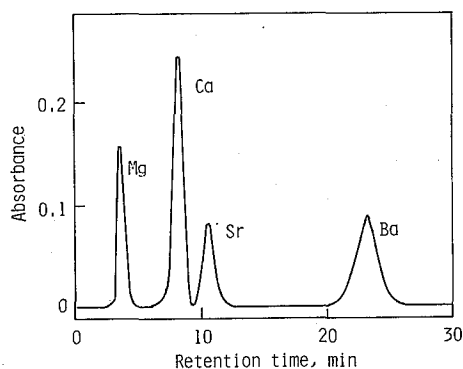


Fig. 6. Separation of alkali earths.

Mg, Ca; 0.5 μ g, Sr; 2.5 μ g, Ba; 25 μ g, eluent; 2.5 M NaCl. Others are the same as in Fig. 5.

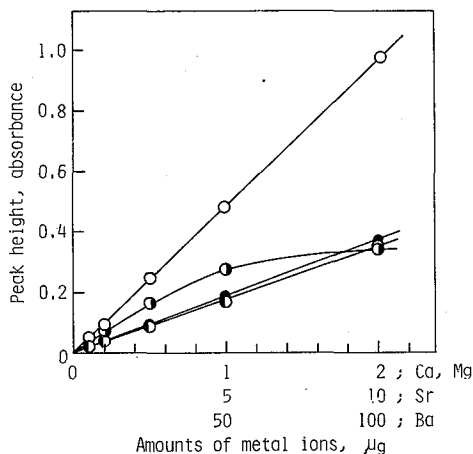


Fig. 7. Calibration curves.

Eluent; 2.5 M NaCl, color forming reagent solution; 6×10^{-5} M PC, 7.5% MeOH, 1.0 M ammonia-ammonium chloride buffer (pH 10.6), flow rate; 0.42 ml/min in eluent, 0.86 ml/min in color forming reagent solution.

●; Mg, ○; Ca, ○; Sr, ●; Ba.

chloride was selected as the eluent.

Chromatograms and Calibration Curves

A typical example of the chromatogram in the alkali earth system is shown in Fig. 6. The elution order is typical of that found for strong cation exchange resin. The time required for the separation of four alkali earth ions was within 25 min.

Figure 7 shows the relationship between the peak height and the amounts of alkali earth ions. Linear relations were obtained in the range of 0.1 to 1 μg for magnesium, 0.05 to 2 μg for calcium, 0.5 to 10 μg for strontium and 5 to 100 μg for barium.

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